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ICP/MS Isotope Ratios: Identification of Atmospheric
Emissions of Metals

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Identification of sources of pollutants is important for assessing environmental quality, and for planning and implementing abatement strategies. Reliable source identification at locations distant from the sources is usually difficult to achieve because of the large numbers of distinct sources emitting chemically-identical pollutants.

Analytical methods have been developed by the Ontario Ministry of the Environment which exploit slight differences in the isotopic composition of heavy metals from different sources to identify the fraction of these elements from each source. The results have been applied successfully to source apportionment of Pb in atmospheric aerosol samples from Dorset, Ontario, and a number of other locations. An exploratory study using Cd isotopes has also been carried out.

The approach required an analytical method with high sensitivity and specificity, low detection limits, and a low per sample cost. These conditions were satisfied by the use of ICP/MS (inductively-coupled plasma/mass spectrometry), which has detection limits on the order of 0.02 ppb for Pb. Method detection limits are actually determined by trace levels of metals in the sampling media, and are approximately 2.0 ppb for Pb, equivalent to 0.05 ng-m⁻³ of Pb in a 24-hour aerosol sample.

Most of the work to date has focused on the use of the ²⁰⁶Pb/²⁰⁷Pb isotope ratio in atmospheric samples. Because of a fortuitous combination of geological and economic factors, there is a significant difference in this ratio in Pb from United States and Canadian automotive exhaust, which remains the largest source (60% - 70%) of Pb in the North American environment. The ²⁰⁶Pb/²⁰⁷Pb ratio is determined by the geological age of the ore body from which the Pb was extracted. Pb compounds are added to automotive fuel as anti-knocking agents, which are eventually released into the atmosphere as combustion products. Primary Pb

sources for Canadian refineries are located in British Columbia and New Brunswick, with $^{206}\text{Pb}/^{207}\text{Pb}$ ratios around 1.15, while US refineries use lead ores with $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the range 1.20-1.25.

Aerosol samples collected in various Ontario and US cities around the Great Lakes confirmed the validity of the distinct ratios. Further proof was obtained from analysis of daily aerosol samples collected at Dorset by the Atmospheric Environment Service of Canada in the autumn of 1984 and the spring of 1986. The Lagrangian air parcel back-trajectories associated with each sample showed that the observed $^{206}\text{Pb}/^{207}\text{Pb}$ ratios were consistent with the likely sources of the atmospheric Pb.

A simple receptor model was devised which used the mean $^{206}\text{Pb}/^{207}\text{Pb}$ source ratios to calculate the concentration-weighted fraction of Pb from US and Canadian sources. Approximately 46% of the atmospheric Pb at Dorset in 1984 came from US sources, with 52% from Canadian sources. Stratification of the data further revealed that episodes of high Pb concentrations were due to advection of pollutants from the United States. Observations of unusually low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (<1.15) in the Dorset samples were attributed to emissions from non-ferrous smelters in the Sudbury and/or Noranda Val d'Or regions. These sources accounted for about 2% of the atmospheric Pb observed at Dorset in the autumn of 1984.

Analysis of the $^{112}\text{Cd}/^{114}\text{Cd}$ ratio in the 1986 series of Dorset aerosol samples revealed a variability in the ratio which could not be explained by sampling or analytical variability. Analysis of Cd isotope ratios is complicated by isobaric and oxide interferences; however, the magnitude of these interferences can be calculated and corrections applied. A more serious limitation is the apparent lack of a simple correlation between the Cd isotope ratio and source type or region, as there is for Pb.

Further applications of the Pb isotope apportionment method are being considered, both for routine monitoring purposes and for application to other environmental matrices. Sources of other heavy metals, such as Cd and Hg, may also be identified eventually by their isotopic composition, but these will require further development of the methodology and a better definition of the conditions (eg., local- or regional-scale problems) when they might be employed most successfully.

